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CHEMISTRY.—*Diazo sulfonates.*[1] W. L. HALL and H. D. GIBBS, Hygienic Laboratory, U. S. Public Health Service.

In 1868, about a decade after Griess' epoch making discovery of the diazo compounds, Schmitt and Glutz,[2] while studying the reactivity of these compounds towards various reagents, synthesized the first diazo sulfonates. They observed that the addition of moist diazonium chlorides to concentrated solutions of sodium hydrogen sulfite produced clear yellow solutions which did not evolve nitrogen even when heated to boiling. From diazotized ortho- and paraaminophenol, treated in this manner, they isolated beautiful yellow crystalline compounds having the formula $C_6H_4 \cdot OH \cdot N_2SO_3K$. They concluded that the acid sulfite had condensed with the diazo phenols and predicted that the reaction would be characteristic for all diazo compounds.

Strecker and Römer[3] (1871) studied the behavior of diazo-benzene towards potassium hydrogen sulfite and, as predicted by Schmitt and Glutz, obtained a condensation of the acid sulfite with the diazo compound, but they noted that during the reaction sulfur dioxide was evolved. Their recrystallized compound was colorless and reduced certain metallic salts, and an analysis gave the molecular formula $C_6H_7N_2SO_3K$. They proved that the sulfonic group was not directly attached to carbon and attempted to write a structural formula for the compound, but failed to recognize the simple relationship between their experiments and those of Schmitt and Glutz.

Fischer[4] (1875) seems to be the first to explain the mechanism of

[1] Published by permission of the Surgeon General, U. S. Public Health Service. Received Sept. 2, 1927.

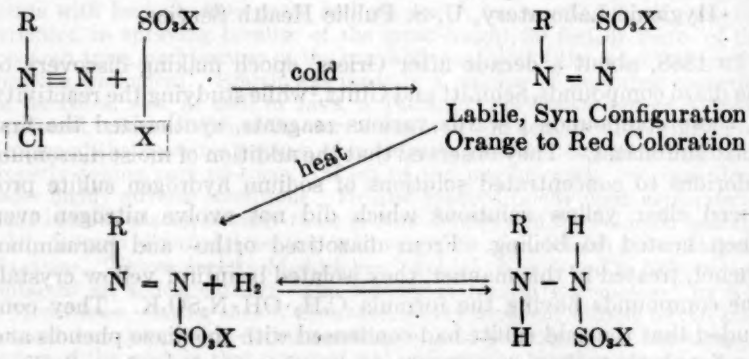
[2] Ber. Deutsch. Chem. Ges. **2**: 51. 1869.

[3] Ber. Deutsch. Chem. Ges. **4**: 784. 1871.

[4] Ber. Deutsch. Chem. Ges. **8**: 589. 1875.

the syntheses. He proved that Schmitt and Glutz's yellow compound and Strecker and Römer's colorless compound were similar in type. In repeating Strecker and Römer's work, Fischer used neutral sulfite and later alkaline sulfite,[5] and obtained a yellow compound whose molecule contained two less hydrogens than found by Strecker and Römer. With oxidizing and reducing agents, Fischer was able to convert a yellow compound into a colorless one and *vice versa*, thereby demonstrating a chemical reversibility.[6]

Diagramatically, the synthesis and reversibility of the diazo sulfonates may be represented by the following equations,[7] where R is an aromatic radical and X a metal.



This property of the diazo sulfonates to undergo reversible oxidation and reduction, and the possibility of measuring their electrode potentials, instigated the syntheses of 10 of these compounds, five of which apparently are new. So far, measurements made of the electrode potentials are not conclusive enough to warrant publication of this phase of the problem.

The part played by the diazo sulfonates in advancing the science

[5] Ann. Chem. 190: 67. 1878.

[6] Although Strecker and Römer noted that when their compound reduced silver nitrate a yellow solution was produced, and from this solution they isolated a yellow silver salt, they were at loss for an explanation as to what had taken place.

[7] Adopting Hantzsch's theories. For a detailed discussion of the stereochemistry of the diazo sulfonates see J. C. CAIN, *The chemistry and technology of the diazo compounds*, Edward Arnold, London, 1920; and LACHMAN, *The spirit of organic chemistry*, p. 216, The Macmillan Co., New York, 1904.

of chemistry has been an important one. E. Fischer's[8] researches on the use of the diazo sulfonates in hydrazine synthesis, first discovered by Strecker and Römer,[9] has indeed proved to be a very fruitful piece of work. The use of the diazo sulfonates by Hantzsch, Bamberger, Blomstrand, and others, as evidence for and against the constitution of diazo salts, has been noteworthy. Many substitution products of the simplest benzene diazo sulfonates were synthesized in the search for a stable molecule of the syn configuration. These researches have thrown some light on the stabilization of such a labile molecule.

The outstanding characteristic of these compounds in the pure state, synthesized as here described, is their surprising stability. The authors have on hand some compounds that gave a check analysis after the lapse of over a year and a half. Apparently, all diazo sulfonates will keep perfectly when not exposed to moisture and excess light. All the sodium or potassium salts containing a single aromatic ring that have either been studied or described are yellow to orange and give like-colored solutions, the color and solubility depending upon ring structure.

Hydrazine sulfonic acids[10] can be prepared from the diazo sulfonates by reduction with zinc dust and acetic acid. By careful recrystallization, avoiding oxidation,[11] colorless crystalline compounds may be obtained.

Like many organic syntheses, the production of the diazo sulfonates is comparatively simple when one has learned from experience the proper procedure. Experiments have shown that success lies in the proper control of the pH. As Fischer showed the Schmitt and Glutz method to be faulty, so do we find the Fischer and subsequent methods inadequate when applied to certain intermediates. One must always bear in mind that at no time during the condensation should sulfur dioxide be liberated. Should this happen there may be obtained a gummy mass or even a tar, which possibly is a mixture of the oxidized and reduced sulfonates, sulphazides, and what not. Only a slight excess of sulfite should be used in certain cases, otherwise disulfonates of type formula $R \cdot NSO_2NaNHSO_2Na$ may be obtained, where R is an aromatic radical, usually containing nitro or sulfonic acid groups.

Since in practically all diazotizations here considered an excess of

[8] Ber. Deutsch. Chem. Ges. 8: 592, 1005. 1875.
[9] Ber. Deutsch. Chem. Ges. 4: 785. 1871.
[10] E. FISCHER. Ber. Deutsch. Chem. Ges. 8: 590. 1875.
[11] H. REISENEGGER. Ann. Chem. 221: 315. 1883.

acid is necessary and at the same time prevents the formation of diazo amido compounds, one is confronted with the problem of obtaining a reaction between the diazonium solution and sulfite without liberating sulfur dioxide. Investigators in the past evaded this difficulty by either isolating the diazonium compound and using neutral or acid sulfite solution, or by adding the diazonium solution directly to sulfite made excessively alkaline. Later workers showed that if after diazotization the excess acid was neutralized near 0° and this solution added to sodium sulfite good results were obtained, but we found the method did not apply in all cases. The following procedure was finally devised and worked excellently where the others had failed. The diazotized solution was added, simultaneously with an amount of sodium hydroxide sufficient to neutralize the excess acid, to the cooled sodium sulfite solution, the rates of adding the alkali and diazonium solutions being such that the pH of the reaction was kept between empirical values and at no time was sulfur dioxide liberated or alkali concentration high enough to cause decomposition.

In all cases, except one, a yield of crystals colored from a brownish orange to almost red, was found to be caused by too great an alkalinity during the reaction.

Whatever the procedure, experience has proved that for good yields high concentrations of all solutions are advisable, and even then salting out of the product is necessary for the very soluble compounds.

EXPERIMENTAL DATA[12]

1-Methylbenzene-2-diazosodiumsulfonate

$$1\text{-}CH_3 \cdot C_6H_4\text{-}2\text{-}N_2SO_3Na$$

To 10.7 grams of commercial ortho toluidine[13] were added 30 cubic centimeters of water and 25 grams of concentrated (36 per cent) hydrochloric acid. Upon cooling, crystals of the hydrochloride separated. Nevertheless at 0° the suspension was easily diazotized with 21 to 24 cubic centimeters of a 36 per cent solution of sodium nitrite. The end-point was determined with starch iodide paper. A beaker containing 52 cubic centimeters of a 25 per cent sodium sulfite solution[14] was surrounded by a salt-ice mixture and the diazotized solution run into the cold sulfite suspension until a spot

[12] The authors are indebted to C. G. Remsburg, Division of Chemistry, Hygienic Laboratory, for the analyses of the following compounds, except the nitrogen determinations which we determined by the combustion method.

[13] Although these quantities are for tenth molal proportions, ten times the amounts, or molal quantities, were found to work equally well.

[14] Sodium sulfite slowly changes to sulfate. It is therefore advisable to make previously a rough analysis. We found it convenient to use an analyzed saturated solution kept in a tightly stoppered bottle.

plate determination showed the reacting solution to have an acidity of about pH 5.6 (deep blue to brom cresol green or just orange red to brom phenol red). Cold 20 per cent sodium hydroxide was next dropped in until the alkalinity increased to about pH 8.2 (yellowish green to thymol blue); more diazotized solution was then added until pH 5.6 was noted, then more alkali until pH 8.2, and so on in alternation until all the diazotized solution was added. At the end the alkalinity of the liquid should be adjusted to about pH 10 (distinctly blue to thymol blue). A total of 6 to 8 cubic centimeters of the 20 per cent alkali is required. With a little experience one can add simultaneously to the sulfite, the alkali and diazotized solution, and still keep within the required pH (5.6 to 8.2) zone. During the reaction beautiful light orange plates separated, which probably were a mixture of the syn compound and crystals of sodium sulfite. The beaker was removed from the ice bath, 10 grams of sodium chloride added, and the whole heated slowly with stirring at 70°. The resulting deep orange red solution was filtered and cooled to 0° with occasional stirring. Clumps of short yellow needles crystallized. These were separated from the mother liquor and purified by three recrystallizations from hot water, in which they were very soluble. The compound was dried at reduced pressure over soda lime-calcium chloride-caustic soda mixture. All subsequent drying of crystals was made in this manner unless otherwise stated.

Analysis:

Calculated for $C_7H_7N_2SO_3Na$: N 12.61, S 14.43
Found: N 12.78, S 14.22

Colorless crystals of the hydrazine sulfonate were prepared by reduction of a hot saturated 25 per cent acetic acid solution of the diazo sulfonate with an excess of zinc dust, heating and stirring on a steam bath until the solution was practically colorless. After filtering and cooling the crystals separated, but no further investigation was made.

1-Methyl-4-sodiumsulfonatebenzene-2-diazosodiumsulfonate

$1\text{-}CH_3\text{-}4\text{-}SO_3Na \cdot C_6H_3\text{-}2\text{-}N_2SO_3Na$

To 18.7 grams (see footnote 13) of commercial 2-aminotoluene-4-sulfonic-acid was added 30 cubic centimeters of water and only 15 grams of concentrated 36 per cent hydrochloric acid. To the suspension, cooled to 0°, 21 to 24 cubic centimeters of a 36 per cent solution of sodium nitrite was added. The diazotized compound was partially insoluble and evidence of its precipitation was noted after one-half of the amount of nitrite had been added. The end-point was determined with starch iodide paper. There was slowly dropped into the yellow diazotized suspension 13 cubic centimeters of a 40 per cent sodium hydroxide solution, forming the sodium salt of the sulfonic acid and neutralizing the excess acid. Although a suspension still persisted, 52 cubic centimeters of a 25 per cent sodium sulfite solution was added, producing a complete solution. At no time was the temperature of the reaction allowed to rise above 10°, and at the end the pH of the solution was about 9.0 (blue to thymol blue). Upon adding 25 grams of sodium chloride, heating to 70°, filtering and cooling, deep yellow, short needles crystallized. These were separated and recrystallized twice from hot water. Great care was exercised in recrystallization since this compound was extremely soluble in hot and cold water. The purified product was dried at 100° and when dry it absorbed moisture very quickly from the atmosphere.

Analysis:
Calculated for $C_7H_6N_2S_2O_6Na_2$: N 8.64, S 19.78
Found: N 8.69, S 19.42

By means of acetic acid and zinc dust reduction, the colorless hydrazine sulfonate was prepared.

1,3-Dimethylbenzene-4-diazosodiumsulfonate

1,3$(CH_3)_2C_6H_3$-4-N_2SO_3Na[15]

To 12.1 grams (see footnote 13) of commercial 4-aminometaxylene was added 30 cubic centimeters of water and 25 grams of concentrated 36 per cent hydrochloric acid. Exactly the same procedure and quantities of nitrite, sulfite, and alkali were used as in making 1-methylbenzene-2-diazosodiumsulfonate. In the present case, however, 25 grams of sodium chloride was added and subsequent heating to 70° caused a slight tarring which we were not able to prevent.

The tar was easily removed in the filtration and gave no further trouble. On cooling the hot solution to 0° bundle-like short orange yellow needles separated. They were filtered, recrystallized from hot water, and dried.

Analysis;
Calculated for $C_8H_9N_2SO_3Na$: N 11.86, S 13.58
Found: N 12.15, S 13.29

By means of acetic acid and zinc dust the compound was reduced to the colorless hydrazine sulfonate. Upon drying, the crystals became slightly pink.

1-Hydroxy-2,6-dichlorobenzene-4-diazosodiumsulfonate

1-HO-2,6-Cl_2·C_6H_2-4-N_2SO_3Na

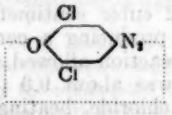
Schmitt and Glutz[16] (1868) in a simple quantitative manner synthesized a dichlorophenoldiazosulfonate. They must, however, have used a 4,6-dichloro-2-aminophenol as their starting material.

We diazotized commercial 2,6-dichloroparaaminophenolsulfate, in the usual manner. The diazotized compound precipitated[17] and the suspension

[15] The synthesis and reduction of this compound showed it to be the most unstable of the series.

[16] Ber. Deutsch. Chem. Ges. 2: 52. 1869.

[17] Paraaminophenol, when diazotized and treated with a sodium hypochlorite solution made according to the method of Raschig (Ber. Deutsch. Chem. Ges. 40: 4586. 1907), substituted two chlorine atoms in the 2,6-position of the ring and gave the same type of precipitate. Indications are that the precipitate was an anhydride having the graphic formula.



Evidence in favor of such a structure is as follows:

Certain diazotized compounds form similar anhydrides, as, for example, diazotized sulfanilic acid. A corresponding precipitate was obtained when 2,6-dibromoparaaminophenol was diazotized whereas its methyl ester was soluble. In the last case the substituted methyl group prevented formation of the anhydride.

was added to a slight excess of the molecular requirement of alkaline sodium sulfite. The sulfite, in this case, was not completely in solution and contained enough 20 per cent sodium hydroxide to neutralize the excess acid used in diazotization. After standing for an hour, with occasional stirring, the whole was heated to 70°, filtered and cooled. The crystallized yellow plates were separated, recrystallized three times from hot water, and dried. The dry compound quickly absorbed moisture from the atmosphere.

Analysis:

Calculated for $C_6H_3N_2Cl_2SO_4Na$: N 9.56, S 10.94, Cl 24.20
Found: N 9.55, S 10.72, Cl 24.14

Upon reduction with zinc dust and acetic acid, the hydrazine sulfonate[18] was prepared in colorless crystals.

1-Hydroxy-2,6-dibromobenzene-4-diazosodiumsulfonate

1-HO-2,6-Br_2-C_6H_2-4-N_2SO_3Na

Böhmer (1881)[19] first made this compound by brominating paradiazophenol with bromine water. He separated the precipitated diazotized product, treated it with sodium hydrogen sulfite and heated. His diazosulfonate contained 2 molecules of water of crystallization. Hantzsch and Davidson (1896)[20] prepared the potassium salt of this diazosulfonate, using potassium sulfite as a sulfonating agent. In repeating Böhmer's work, we found that his method of bromination with bromine water required too large a volume.[21] Therefore we first synthesized 2,6-dibromo-4-aminophenol by the bromination, in an acetic acid solution, of paranitrophenol

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The precipitate was separated and dissolved in 36 per cent hydrochloric acid at 20°. A residue was filtered and the filtrate reduced at 0° with a solution of stannous chloride in 36 per cent hydrochloric acid. The hydrazine hydrochloride, 1-HO-2, 6-Cl_2,C_6H_2-4-$NHNH_2HCl$, so obtained was filtered, dissolved in water, and twice precipitated from its solutions by adding one-half its volume of 36 per cent hydrochloric acid. After drying over caustic soda—soda lime mixture it gave only a poor analysis, and as it was found to be rather unstable even when isolated and dried, no further study was made.

A preliminary report of this hydrazine was presented at the Washington, D. C., meeting of the American Association for the Advancement of Science, Dec. 29, 1924.

[18] Although we were able to obtain the hydrazine hydrochloride by stannous chloride reduction, the Fischer hydrazine sulfonate method gave no results.

[19] Journ. Prakt. Chem. **24**: 453, 465. 1881.

[20] Ber. Deutsch. Chem. Ges. **29**: 1532. 1896.

[21] We used a modified procedure by which a tenth of a mol of diazotized paraaminophenol was easily brominated in a small volume. The brominating solution was prepared as follows: Bromine, 35 grams, was dissolved in a saturated solution of 40 grams of potassium bromide at 20°. The solution was then diluted to a volume of 400 cubic centimeters. When the concentrated bromine solution was added, with stirring, to the diazotized phenol in the presence of much crushed ice, the anhydride of 2,6-dibromo-4-diazophenol was precipitated. The precipitate was separated, dissolved in 36 per cent hydrochloric acid, reduced to the hydrazine, etc. (see footnote 17). The hydrazine hydrochloride, 1-HO-2,6-$Br_2C_6H_2$-4-$NHNH_2HCl$, so obtained, although apparently more stable than the dichloro compound, decomposes slowly in solution and likewise when dry.

Analysis:

Calculated for $C_6H_7ON_2Br_2Cl$: N 8.80
Found: N 9.00

(Möhlau and Uhlman 1895).[22] The 2,6-dibromonitrophenol was reduced at 70° with tin and concentrated hydrochloric acid and the tin precipitated with hydrogen sulfide. The 2,6-dibromo-4-aminophenolhydrochloride when diazotized precipitated, and the suspension was added directly to a 10 per cent excess over the calculated quantity of alkaline sodium sulfite suspension, heated, cooled and crystallized. The purified diazo sulfonate, when dried at reduced pressure, did not contain two molecules of water of crystallization, as did Böhmer's compound.

Analysis:

Calculated for $C_6H_3N_2Br_2SO_4Na$: N 7.33, S 8.39, Br 41.85
Found: N 7.36, S 7.71, Br 42.15

Zinc dust and acetic acid reduced the compound to the colorless hydrazine sulfonate.[23] The isolated crystals were not analyzed.

1-Methoxy-2,6-dibromobenzene-4-diazosodiumsulfonate

1-CH_3O-2,6-Br_2·C_6H_2-4-N_2SO_3Na

Hantzsch and Pohl[24] (1902), after the method of Stadel[25] (1882) and Korner[26] (1874), synthesized 2,6-dibrom-4-anisidine by the use of methyl iodide in the mythelation of the silver salt of 2,6-dibromo-4-nitrophenol and reducing the methylated compound. The resulting dibromoanisidine was specially diazotized and from the isolated diazonium nitrate, both the syn and antidiazotates were made. They found the two isomeric diazotates to have approximately the same stability. Apparently they did not extend their researches into the corresponding diazosulfonates. Since our interest lay in the antidiazosulfonate we synthesized it by methylating 2,6-dibromo-4-nitrosodium-phenolate by means of dimethylsulfate in several different ways. The methylation of this compound is the subject of an interesting study which we hope to describe in a future article.

The compound was recrystallized at 60° from ethyl alcohol containing 10 per cent, by volume, of acetone and one per cent of sodium hydroxide. A portion of this product when further crystallized from ethyl alcohol gave a melting point of 122.7° against 122.6° (uncorrected) in the literature.[26] Another portion recrystallized from chloroform gave a melting point of 123.7° (uncorrected). The compound sublimed very slowly at 95° and the sublimed product likewise gave a melting point of 123.7° (uncorrected).

Reduction to the 2,6-dibromoanisidine was accomplished by treating 104 grams of the dibromonitroanisol with 275 cubic centimeters of 36 per cent hydrochloric acid and 80 grams of granulated tin. The tin was added in small portions to the continuously stirred suspension. If the temperature was kept between 75° to 85°, the reduction proceeded satisfactorily

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Böhmer (Journ. Prakt. Chem. **24**: 472. 1881) tried to synthesize this hydrazine by reducing the isolated diazonium compound with zinc dust and acetic acid. He proved its presence in a qualitative way but because of instability never isolated it.

A preliminary report on this hydrazine was made at the Washington, D. C., meeting of the American Association for the Advancement of Science, Dec. 29, 1924.

[22] Ann. Chem. **289**: 94. 1896.

[23] Attempts to prepare the hydrazine hydrochloride by the Fischer method were unsuccessful.

[24] Ber. Deutsch. Chem. Ges. **35**: 2969. 1902.

[25] Ann. Chem. **217**: 70. 1883.

[26] Gazz. chimi ital. **4**: 390. 1874.

and completion was noted after 3 to 4 hours. At the end there was a brown solution having approximately a volume of 600 cubic centimeters at 102°. The tin double salt crystallized upon cooling, was separated, dissolved in hot water, and the tin was precipitated by leading hydrogen sulfide into the hot solution. The hydrochloride of the dibromoanisidine crystallized from the filtered, hot, tin-free solution. A portion was recrystallized from 20 per cent hydrochloric acid, dried[27] and analyzed.

Analysis:

Calculated for $C_7H_8ONBr_2Cl$: N 4.41
Found: N 4.42

Unlike Hantzsch and Pohl we diazotized the dibromoanisidine in the usual manner except that a decided excess of hydrochloric acid was necessary.[28] For 32 grams of 2,6-dibromo-4-anisidine hydrochloride there were required 200 cubic centimeters of water and 25 grams of 36 per cent hydrochloric acid. This thick suspension was diazotized at 0° to 5° by very slowly dropping in 24 to 26 cubic centimeters of a 36 per cent solution of sodium nitrite. The end-point in this case could not be determined since an excess of nitrite was needed to take care of small lumps of the undiazotized material which seem to react very slowly toward the end. A slight precipitate persisted which was possibly a trace of the anhydride of the unmethylated compound and a small amount of the diazoamino compound. This precipitate was removed by filtration. The excess acid, in the clear diazotized solution,[29] was neutralized by slowly dropping in, with stirring, 60 to 65 cubic centimeters of 10 per cent sodium hydroxide solution. A yellow precipitate was formed. The pH of the suspension had to be adjusted between 5.6 and 5.8 (orange red to brom phenol red) for a successful sulfonation, then 52 cubic centimeters of a 25 per cent solution of sodium sulfite was slowly run in. The contents of the beaker set almost solid, but after a slow heating to 90° a dark orange red solution containing a slight precipitate was produced. The solution was filtered and cooled, whereupon beautiful yellow plates were obtained. The crystals were separated, recrystallized from hot water and dried.

Analysis:

Calculated for $C_7H_5N_2Br_2SO_4Na$: N 7.08, S 8.10, Br 40.37
Found: N 7.06, S 7.50, Br 40.11

By reduction with zinc dust and acetic acid the corresponding colorless hydrazine sulfonate was prepared. The isolated crystals were not analyzed.

[27] If the compound was dried at 100° it partly sublimed.

[28] In several instances where the acid was not in sufficient excess a yellow insoluble precipitate was formed. Analysis of this precipitate, after recrystallizing from benzene, indicated the formation of the diazoamino compound having a melting point of 187.7°, uncorrected.

Analysis:

Calculated for $C_{14}H_{11}O_2N_3Br_4$: Br 55.81, N 7.34
Found: Br 56.37, N 7.74

[29] When this solution was treated with stannous chloride dissolved in 36 per cent hydrochloric acid, colorless crystals of the hydrazine hydrochloride precipitated. These were filtered, and an attempt to purify them was unsuccessful because all solvents tried caused a decomposition with an evolution of nitrogen. The isolated crystals, when dried over caustic soda, were found to be stable.

1-Hydroxybenzene-4-diazosodiumsulfonate

$1\text{-}HO\cdot C_6H_4\text{-}4\text{-}N_2SO_3Na$

The potassium salt of this compound was first made and described by Schmitt and Glutz[30] (1868) as containing water of crystallization. As previously mentioned they used potassium hydrogen sulfite as the sulfonating agent. Fischer[31] (1877) made the compound by the use of alkaline sulfite. Reisenegger[32] (1883) showed that Schmitt and Glutz's compound did not contain a molecule of water of crystallization. We made the sodium salt of this diazo sulfonate by adding a diazotized solution of paraaminophenol to a 10 per cent excess over the calculated quantity of alkaline sodium sulfite. After heating to 70°, filtering and cooling, there was produced a mass of canary yellow crystals. These were separated, recrystallized from hot water three times and dried.

Analysis:

Calculated for $C_6H_5N_2SO_4Na$: N 12.50, S 14.31, Na 10.26
Found: N 12.43, S 14.40, Na 10.43

Like Reisenegger[33] (1883) we obtained the colorless hydrazine sulfonate upon reduction with zinc dust and acetic acid. The addition of ethyl alcohol to a cold saturated solution of this compound caused it to crystallize. No further study was made.

1-Ethoxybenzene-4-diazosodiumsulfonate

$1\text{-}C_2H_5O\cdot C_6H_4\text{-}4\text{-}N_2SO_3Na$

Altschul[34] (1892) first synthesized this compound by treating diazotized paraaminophenetol with alkaline sodium sulfite. We likewise prepared it with alkaline sodium sulfite.

Analysis:

Calculated for $C_8H_9N_2SO_4Na$: N 11.11, S 12.72
Found: N 11.12, S 12.51

By a method similar to that of Altschul[35] (1892), with zinc dust and acetic acid, we easily reduced the compound to the colorless hydrazine sulfonate. The isolated crystals were not analyzed.

1-Dimethylaminobenzene-4-diazosodiumsulfonate

$1\text{-}(CH_3)_2N\cdot C_6H_4\text{-}4\text{-}N_2SO_3Na$

Stollé[36] (1912) made this compound by isolating the diazonium chloride of diazotized paraaminodimethylaniline, dissolving it in water, and adding a solution of sodium bisulfite. Our method of preparation was perhaps a little simpler inasmuch as the diazotized compound does not have to be isolated. To 17.5 grams of paraaminodimethylaniline hydrochloride dissolved in 300 cubic centimeters of water, was added 15 grams of 36 per cent hydrochloric acid. The solution was diazotized at 0° by slowly adding

[30] Ber. Deutsch. Chem. Ges. **2**: 51. 1869.
[31] Ann. Chem. **190**: 73. 1877.
[32] Ann. Chem. **221**: 316. 1883.
[33] Ann. Chem. **221**: 317. 1883.
[34] Ber. Deutsch. Chem. Ges. **25**: 1843. 1892.
[35] Ber. Deutsch. Chem. Ges. **25**: 1844. 1892.
[36] Ber. Deutsch. Chem. Ges. **45**: 2681, 2682. 1912.

about 42 cubic centimeters of an 18 per cent sodium nitrite solution. The end-point was determined by starch iodide paper. The diazotized solution was slowly run into an alkaline sodium sulfite mixture (52 cubic centimeters of 25 per cent sodium sulfite plus 28 cubic centimeters of a 10 per cent solution of sodium hydroxide). The pH of the resulting brown suspension was about 9.0 (blue to thymol blue). Heating to 90°, filtering, and the addition of 70 grams of salt yielded brown needles. These were recrystallized and purified by boiling with decolorizing carbon. The pure, deep brownish orange crystals were dried and analyzed.

Analysis:

Calculated for $C_8H_{10}N_2SO_3Na$: N 16.73, S 12.77
Found: N 16.41, S 12.44

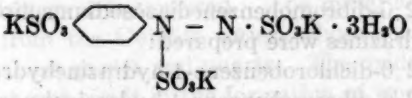
We found this diazo sulfonate to be the least stable in solution. Even in the dark, a hundredth molecular solution decomposed with the separation of a precipitate.

According to Stollé[37] (1912) zinc dust and acetic acid reduce the diazosulfonate to paraaminodimethylaniline.

1-Sodiumsulfonatebenzene-4-diazosodiumsulfonate

1-$NaSO_3 \cdot C_6H_4$-4-N_2SO_3Na

Strecker and Römer[38] (1871) tried to synthesize this diazosulfonate but did not isolate the compound. Fischer[39] (1877) isolated a light yellow compound, apparently a mixture of oxidized and reduced forms. Pechman[40] (1895) prepared the potassium salt, precipitating it with alcohol. He pointed out that in the presence of an excess of sulfite the diazodisulfonate



could be obtained. We confirmed this in a qualitative way. Hantzsch and Schmiedel[41] (1897) also prepared the potassium salt of the diazomonosulfonate but found it to contain a molecule of water of crystallization. We synthesized the sodium salt of this diazosulfonate as follows.

To 96 grams of sulfanilic acid, 125 grams of 36 per cent hydrochloric acid and 200 cubic centimeters of water were added. This was diazotized at 5° with about 115 cubic centimeters of a 36 per cent sodium nitrite solution. The diazotized compound precipitated as the anhydride, colorless needles. Into the cooled suspension 70 cubic centimeters of 40 per cent sodium hydroxide solution was dropped until the pH was 9.8 (blue to thymol blue). The approach to the end-point was noted by a yellow appearance of the diazotized compound. Sodium sulfite, 260 cubic centimeters of a 25 per cent solution, was slowly added and a deep orange solution obtained. Then

[37] Ber. Deutsch. Chem. Ges. **45**: 2680. 1912.
[38] Ber. Deutsch. Chem. Ges. **4**: 784. 1871.
[39] Ann. Chem. **190**: 76. 1877; Ber. Deutsch. Chem. Ges. **8**: 593. 1875.
[40] Ber. Deutsch. Chem. Ges. **28**: 863. 1895.
[41] Ber. Deutsch. Chem. Ges. **30**: 79. 1897.

100 grams of salt was added and the solution heated to 90°, whereupon a partial separation of the diazo sulfonate took place. Cooling to 5° yielded yellow needles, which were separated and purified by precipitation from a water solution with an equal volume of methyl alcohol. The compound was dried at 100° and then analyzed.

Analysis:

Calculated for $C_6H_4N_2S_2O_6Na_2$: N 9.03, S 20.67
Found: N 9.02, S 20.02

Like Pechman[42] (1895), we obtained the colorless hydrazine sulfonate by reduction with zinc dust and acetic acid. The isolated crystals were purified by methyl alcohol precipitation, and a final washing with absolute methyl alcohol. They were dried at 60°.

Analysis:

Calculated for $C_6H_6N_2S_2O_6Na_2$: N 8.97
Found: N 8.90

SUMMARY

A brief review of the historical development and uses of the diazo sulfonates is given.

In pursuit of certain definite diazo sulfonates 10 were prepared and apparently the following five are new:

1-Methylbenzene-2-diazosodiumsulfonate
1-Methyl-4-sodiumsulfonatebenzene-2-diazosodiumsulfonate
1,3-Dimethylbenzene-4-diazosodiumsulfonate
1-Hydroxy-2,6-dichlorobenzene-4-diazosodiumsulfonate
1-Methoxy-2,6-dibromobenzenediazosodiumsulfonate

Three new hydrazines were prepared:

1-Hydroxy-2,6-dichlorobenzene-4-hydrazinehydrochloride
1-Hydroxy-2,6-dibromobenzene-4-hydrazinehydrochloride
1-Methoxy-2,6-dibromobenzene-4-hydrazinehydrochloride

A new diazoamino compound was prepared:

1-Methoxy-2,6-dibromobenzene-4-diazoamino-4′-methoxy-3′,5′-dibromobenzene

MINERALOGY.—*"Blythite" and the manganese garnet from Amelia, Virginia.*[1] EARL V. SHANNON, U. S. National Museum.

In analyzing spessartite or spessartite-bearing garnets during the past several years the writer has at times found difficulty in obtaining an exact agreement of the results of analyses with the general garnet formula, $3RO \cdot R_2O_3 \cdot 3SiO_2$. When the manganese in many garnets

[42] Ber. Deutsch. Chem. Ges. 28: 868. 1895.

[1] Published by permission of the Acting Secretary of the Smithsonian Institution. Received September 7, 1927.

high in content of this element is all calculated as manganous oxide the bivalent bases are a little too high and the trivalent oxides correspondingly low. This fact led some time ago to the supposition that manganese in garnets might, like iron, exist in two states of oxidation, bivalent and trivalent, and that there might be small amounts of an unnamed garnet molecule in which the trivalent alumina is replaced by manganic manganese. Although practically convinced that such a molecule exists, the writer has felt disinclined to put foward such a conclusion without experimental proof, and has held the matter in abeyance pending the working out of a suitable method for the determination of manganic manganese in a silicate as insoluble as garnet. The problem was discussed orally with Drs. Clarence S. Ross, Waldemar T. Schaller, Henry S. Washington and Edgar T. Wherry. The present writer was consequently much interested when his attention was directed by Drs. Ross and Schaller to the recent article on garnets by Fermor[2] in which he recognizes and names the following new molecules:

$3FeO \cdot Fe_2O_3 \cdot 3SiO_2$ = Skiagite
$3MnO \cdot Fe_2O_3 \cdot 3SiO_2$ = Calderite
$3MnO \cdot Mn_2O_3 \cdot 3SiO_2$ = Blythite

Fermor found "blythite," named for the analyst, T. R. Blyth, formerly assistant curator of the Geological Survey of India, in only one of the Indian garnets analyzed. The material is orange-red to orange, and is from the Gondite series, whose rocks are composed largely of manganese garnet and quartz. The oxidation and decomposition of the garnet result in the formation of workable manganese ores, and the garnet rock is thrown by the thousands of tons on the dumps of the manganese mines.[3] The locality of the analyzed material was Chargaon, Nagpur. The analysis follows:

MANGANESE GARNET FROM NAGPUR, INDIA

(T. R. Blyth, analyst)

	Per cent
SiO_2	34.71
Al_2O_3	8.05
Fe_2O_3	8.38
MnO	38.83
MgO	5.40
CaO	4.97
BaO	trace
	100.34

[2] L. LEIGH FERMOR, *On the composition of some Indian garnets.* Records Geol. Surv. India **49**: pt. 2: 191–207. 1926.

[3] L. LEIGH FERMOR. Mem. Geol. Surv. India **37**: 167–168. 1909.

This analysis is interpreted by Fermor in terms of mineral molecules as follows:

		Per cent
Pyrope	$3MgO \cdot Al_2O_3 \cdot 3SiO_2$	18.78
Almandite	$3FeO \cdot Al_2O_3 \cdot 3SiO_2$	none
Spessartite	$3MnO \cdot Al_2O_3 \cdot 3SiO_2$	17.68
Grossularite	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$	none
Andradite	$3CaO \cdot Fe_2O_3 \cdot 3SiO_2$	16.01
Calderite	$3MnO \cdot Fe_2O_3 \cdot 3SiO_2$	12.81
Blythite	$3MnO \cdot Mn_2O_3 \cdot 3SiO_2$	34.72
		100.00

Since the material is not near the pure end-member, it is called "magnesia-blythite" by Fermor. The specific gravity is given as 4.15 to 4.20. Unfortunately no indices of refraction are given for any of the garnets described in the paper.

While examining the analyses of garnet in the literature the writer noted that the manganese garnet from Amelia, Virginia, according to the analysis quoted by Dana[4] from Bradbury[5] (through Fontaine[6]), showed very low alumina and high manganese content. It was accordingly decided to subject this garnet to a reexamination, to see what information it might yield concerning the possible existence and characteristics of such a molecule as "blythite."

Bradbury's analysis indicates the Amelia garnet to contain only 12.63 per cent of alumina whereas pure spessartite requires 20.6 per cent to conform with the formula. According to Fontaine's description the garnet was found on the walls of a large cavity discovered in pit No. 2 of the Rutherford mica mine. It is in angular masses loosely deposited in the interstices between broad, platy crystals of the clevelandite variety of albite, the garnet being younger than the albite and associated with still younger helvite. The material is stated to be pale pink to flesh-red or, in some fragments, brownish-purple. The fusibility is 3; hardness 6.5; specific gravity 4.20. The analysis and ratios, all manganese being stated as MnO, are as follows:

[4] E. S. DANA, *System of mineralogy*, 6th ed., spessartite anal. 1, p. 442. 1895.
[5] C. M. BRADBURY. Chem. News **50**: 120. 1884.
[6] W. M. FONTAINE, *Notes on the occurrence of certain minerals in Amelia County, Va.* Am. Journ. Sci. 3d. ser. **25**: 335. 1883.

ANALYSIS AND RATIOS OF SPESSARTITE

(C. M. Bradbury, analyst)

	Per cent	Ratios		
SiO_2	36.34	.603	.603	.121 × 5
Al_2O_3	12.63	.124	.124	.124 × 1
Fe_2O_3	——	——		
FeO	4.57	.064		
MnO	44.20	.623	.726	.121 × 6
MgO	.47	.012		
CaO	1.49	.027		
	99.70			

This analysis gives rather exactly the formula $6MnO \cdot Al_2O_3 \cdot 5SiO_2$, which certainly cannot be the correct formula for a garnet. Either the mineral is new, the manganese is largely in the manganic form, or there is a serious error in the analytical work. The material was apparently pure, however, and the analytical work appears superficially to be of high grade. If, in the interpretation of the analysis, enough manganese be calculated as Mn_2O_3 to make the ratio for R_2O_3 one-third the ratio for SiO_2, the following results are obtained:

	Per cent	Ratios		
SiO_2	36.34	.603	.603	.201 × 3 (1.00 × 3)
Al_2O_3	12.63	.124	.201	.201 × 1 (1.00 × 3)
Mn_2O_3	12.16	.077		
FeO	4.57	.064		
MnO	33.27	.469	.572	.191 × 3 (.95 × 3)
MgO	.47	.012		
CaO	1.49	.027		
	100.93			

The recalculated figures agree better with the garnet formula, and the mineral molecules, calculated from the bivalent bases, are:

Name	Formula	Mol. weight	Ratio	Per cent
"Blythite"	$3MnO \cdot Mn_2O_3 \cdot 3SiO_2$	551.55	.077	42.47
Spessartite	$3MnO \cdot Al_2O_3 \cdot 3SiO_2$	495.89	.079	39.17
Almandite	$3FeO \cdot Al_2O_3 \cdot 3SiO_2$	498.65	.021	10.40
Grossularite	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$	451.37	.004	1.81
Pyrope	$3MgO \cdot Al_2O_3 \cdot 3SiO_2$	404.06	.009	3.64
				97.56

Recalculating to 100 per cent and prorating the specific gravity, we have:

	Per cent	Proportional specific gravity
"Blythite"	43.53	.4353y
Spessartite	40.15	1.6783
Almandite	10.73	.4560
Grossulaite	1.86	.0657
Pyrope	3.73	.1309
	100.00	$2.3309 + .4353y$

The values for index of refraction and specific gravity of the end-members of the garnet group used in the foregoing and the following interpretations are those of Ford,[7] who derived the following constants for the garnet molecules:

	Index (n)	*Specific gravity*
Spessartite	1.800	4.180
Almandite	1.830	4.250
Grossularite	1.735	3 530
Pyrope	1.705	3 510
Andradite	1.895	3.750

Assuming then that the analysis and the determination of the specific gravity for the Amelia garnet are correct, and that the interpretation given correctly represents the garnet, the specific gravity of the pure "blythite" may be calculated from the data given above by the following simple equation in which y is the specific gravity of "blythite:"

$$\begin{aligned} .4353y + 2.3309 &= 4.2000 \\ .4353y &= 1.8691 \\ y &= 4.294 \end{aligned}$$

The specific gravity thus derived for the pure "blythite," 4.294, would make it the heaviest of the common garnets.

If the index of refraction of an analyzed garnet is known, the index of an unknown end-member may be calculated by the same method as for the specific gravity. The analysis and determinations of the physical constants, however, must be highly accurate for the values thus obtained to be of value.

In order to check the published analysis of the Amelia mineral and to secure an analysis of material which could be examined optically, a lot from the U. S. National Museum collections was selected for study. This lot (Cat. No. 47,705), received in March, 1888, as a gift from Dr. George F. Kunz, consisted of five pieces of practically pure garnet having an aggregate weight of over half a pound (265 grams), the largest piece measuring 6 by 4 by 2 centimeters and weighing about 95 grams. The masses are hackly and preserve bladed molds of some platy mineral, probably clevelandite, which has been leached out. The natural unbroken surfaces of the mineral are partly coated with an olive-green clayey substance and show

[7] W. E. Ford, *A study of the relations existing between the chemical, optical, and other physical properties of the members of the garnet group.* Am. Journ. Sci. 4th ser. 40: 33-49. 1915.

delicate parallel tracings intersecting at the angles of the faces of the rhombic dodecahedron. No other substances are attached to the garnet and it is ideally pure and free from inclusions. The specimens range in color from light to deep reddish amber, are transparent, and have a greasy to resinous luster and conchoidal fracture. In parts the material approaches gem quality. The specific gravity is 4.153, high enough to be noticeable in handling. When crushed, screened, and examined under the polarizing microscope, the sample was found very pure, homogeneous, colorless, and completely isotropic with an index of refraction of 1.794 ± 0.002. The powder screened through 200-mesh is almost white.

Upon analysis the following results were obtained, all manganese being stated as MnO:

NEW ANALYSIS OF GARNET FROM AMELIA, VA.

(Earl V. Shannon, analyst)

	Per cent	Ratios		
SiO_2	35.76	.593	.593	.198 × 3
TiO_2	trace	—	—	
Al_2O_3	17.38	.170	.176	.176 × 1
Fe_2O_3	.92	.006		
FeO	4.90	.068	.638	.213 × 3
CaO	1.66	.030		
MgO	.22	.006		
MnO	37.98	.535		
H_2O	.58			
	99.40			

The ratios are not in exact agreement with the garnet formula. By adding .022 to the ratio for R_2O_3 and subtracting the equivalent .044 from the ratio for R″O the results agree exactly. The recalculated analysis and ratios are then:

	Per cent	Ratios		
SiO_2	35.76	.593	.593	.198 × 3
TiO_2	trace			
Al_2O_3	17.38	.170	.198	.198 × 1
Fe_2O_3	.92	.006		
Mn_2O_3	3.47	.022		
FeO	4.90	.068	.595	.198 × 3
CaO	1.66	.030		
MgO	.22	.006		
MnO	34.86	.491		
H_2O	.58			
	99.75			

Calculated as mineral molecules the revised analysis gives:

	Mol. wt.	Ratio	Per cent	Proportional index	Proportional specific gravity
Spessartite	495.89	.142	70.41	1.2674	2.9431
"Blythite"	551.55	.022	12.13	.1213n	.1213x
Almandite	498.65	.023	11.47	.2099	.4875
Andradite	508.79	.006	3.05	.0578	.1144
Grossularite	451.37	.004	1.81	.0314	.0639
Pyrope	404.06	.002	.81	.0138	.0284
		.199	99.68	1.5803 +.1213n	3.6673 +.1213x

For the specific gravity, x:

$$.1213x + 3.667 = 4.153$$
$$.1213x = .486$$
$$x = 4.01$$

By the same method, for the index n:

$$.1213n + 1.5803 = 1.797$$
$$.1213n = .2137$$
$$n = 1.761$$

The values just found for specific gravity and index must, however, be considered as only of academic interest and not conclusive, owing to the small proportion of the "blythite" constituent.

There is one other analysis of the Amelia garnet available, that published by Clarke.[8] The mineral is described as brilliant brownish-red masses of considerable size, and although some of the material is dark, the specimen analyzed was very light in color. Like the material in the National Museum, it was received from Dr. George F. Kunz, and was doubtless from the same original lot. The analysis gave the following results and ratios:

ANALYSIS OF GARNET FROM AMELIA, VA.

(F. W. Clarke, analyst)

	Per cent	Ratios		
SiO_2	35.35	.586	.586	.195 × 3
Al_2O_3	20.41	.210	.227	.227 × 1
Fe_2O_3	2.75	.017		
FeO	1.75	.024	.587	.196 × 3
MnO	38.70	.546		
CaO	.94	.017		
MgO	none			
Ign.	.27			
	100.17			

[8] F. W. Clark, *Spessartite from Amelia County, Va.* U. S. Geol. Surv. Bull. **60**: 129. 1890.

In this case the trivalent bases—alumina and ferric iron—are decidedly higher in percentage than the garnet formula requires, although the silica and bivalent bases are in good agreement with each other. Ford used Clarke's analysis but saw fit to disregard that of Bradbury. The index of refraction and specific gravity accepted by Ford were determined by him for a sample furnished by Dr. Kunz, not for Clarke's analyzed material. The values are 1.8008 and 4.255 respectively.

It becomes pertinent now, after a perusal of the three foregoing analyses, to inquire into the reason for the difference between the results obtained by Bradbury and those of the two subsequent analyses. Either there are garnets from the same locality of distinctly different composition or Bradbury's analysis is in error in the amounts of alumina and manganese oxide determined. Opposed to the first possibility are the facts that all of the specimens are alike in external characters and associations, all came from the same place at about the same time, and probably all from the same pocket. Fontaine gives the specific gravity as 4.20; Ford measured 4.255; and the material analyzed by the writer, as the mean of three determinations, supplied the value 4.153, indicating only moderate variation in composition. Two other specimens with the same catalogue number as the writer's analyzed sample and from the same lot show the garnet in the interstices of beautiful, platy albite masses. Although of various shades of color, this garnet is all identical in index of refraction with the analyzed material. It appears then, highly improbable that there is more than one garnet in the various analyzed lots under consideration.

The second possibility, analytical error, must be considered. Improbable as it may at first appear, it is very easy indeed to confuse aluminum and manganese in analyzing spessartite. It is almost universal practice to separate these constituents, when the manganese is high in amount, by making the first precipitation by the basic acetate method. This consists of adding an excess of an alkali acetate to the cold neutral solution of the chlorides. No precipitation occurs but the following reaction is believed to take place in the cold solution.

$$AlCl_3 + 3NaC_2H_3O_2 = 3NaCl + Al(C_2H_3O_2)_3$$

(soluble)

On boiling a very voluminous precipitate of basic aluminium acetate separates out thus:

$$Al(C_2H_3O_2)_3 + 2HOH \rightleftharpoons Al\begin{cases} OH \\ OH \\ C_2H_3O_2 \end{cases} + 2HC_2H_3O_2$$

(insoluble)

This second reaction is reversible, and if the solution is allowed to cool the precipitate of basic aluminium acetate redissolves. It is therefore necessary to exercise the utmost care to filter the precipitate at boiling and to recover alumina from the filtrate. Otherwise alumina which passed through the filter may be thrown out as an unsuspected impurity in the manganese sulphide of the succeeding separation and may be weighed with the manganese pyrophosphate. The analysis may still foot-up fairly well and the error may pass unnoticed. As a demonstration of this the writer ran an analysis of a massive spessartite from Connecticut which is to be described in another paper. With the exercise of every precaution to avoid loss of aluminum this analysis gave 20.48 per cent of Al_2O_3. Carelessly rerun, with the basic acetate precipitate allowed to cool and without special recovery of alumina from the filtrate, this same mineral gave only 9.64 per cent of Al_2O_3. It seems quite likely that this explanation accounts for Bradbury's results, and one is inclined to wonder whether the single analysis of the "magnesia blythite" from India, with its high percentage of manganese, may not have a similar explanation. An error of one per cent in the determination of alumina in the analysis would cause an error of 5.41 per cent in the "blythite" in the calculation of the mineral molecules—a large factor wherewith to multiply the error in the analysis.

In conclusion, while the evidence available seems to favor the inference that a "blythite" molecule enters into some mixed crystals of garnet to some extent, the mineral cannot be considered as firmly established until a satisfactory analytical procedure for the determination of manganic manganese in garnet is developed and used on a garnet possessing a considerable content of the manganic molecule.

GEOLOGY.—*An* Acanthoceras rhotomagense *fauna in the Cretaceous of the Western Interior.*[1] JOHN B. REESIDE, JR., U. S. Geological Survey.

Ammonites belonging to the genus *Acanthoceras* in the strict sense, that is, to the group of *A. rhotomagense* Defrance, have been reported from the Woodbine sand and basal Eagle Ford clay of Texas.[2] They have not been recorded, so far as the writer knows, in the literature dealing with the Cretaceous of the Western Interior province. A note of two localities in this region where *Acanthoceras* aff. *A. rhotomagense* occurs is therefore of interest to students of Cretaceous stratigraphy and faunas.

One locality, in south-central Colorado, found by G. K. Gilbert, many years ago lies 1½ miles west of the head of Rock Canyon, in Pueblo County southwest of Pueblo, and the horizon of the fossils is in the Graneros shale about 60 feet above the Dakota sandstone. Most of the species associated with the *Acanthoceras* are undescribed pelecypods and gastropods, though unnamed species of *Turrilites* and *Mammites* (*Pseudaspidoceras*), and an engonoceratid are also represented by fragmentary or somewhat distorted specimens. The next underlying marine fauna is in the Purgatoire formation, beneath the Dakota sandstone, and is composed of Comanchean species. The next overlying fauna is in the Greenhorn limestone, about 150 feet higher in the section, though the intervening part of the Graneros shale has yielded *Exogyra suborbiculata* Lamarck, a small *Ostrea*, and *Inoceramus labiatus* Schlotheim. The Greenhorn limestone is 25 feet thick and contains *Inoceramus labiatus*, a new species of *Thomasites*, *Helicoceras corrugatum* Stanton, *Baculites gracilis* Shumard, *"Acanthoceras" coloradoense* Henderson, and *Metoicoceras whitei* Hyatt. Two hundred feet higher in the section, at the top of the Carlile shale, a fauna with

[1] Published by permission of the Director, U. S. Geological Survey. Received Oct. 1, 1927.

[2] RUDOLF LASSWITZ, *Die Kreide-ammoniten von Texas* (*Collectio F. Roemer*). Geol. Pal. Abh. **10**: 237. 1904.

GAYLE SCOTT, *Études stratigraphiques et paléontologiques sur les terrains crétacés du Texas* p. 136. Grenoble, 1926.

GAYLE SCOTT, *The Woodbine sand of Texas interpreted as a regressive phenomenon.* Bull. Am. Ass. Petr. Geol. **10**: 617. 1926.

Prionocyclus wyomingense Meek, *Ostrea lugubris* Conrad, and *Scaphites warreni* Meek and Hayden occurs. An expected intermediate fauna with *Prionotropis woolgari* Mantell (of Meek) has not been recognized.

The second locality, in middle western Colorado, about 7 miles west of Delta in Delta County, was first found by G. H. Stone and later rediscovered by H. J. Weeks. Here the horizons are in the upper sandstone and upper shale of the Dakota (?) sandstone, the lowest marine beds in the local Cretaceous section. The specimens of *Acanthoceras* are very rare and are accompanied only by an *Inoceramus* of the group of *I. crippsi* close to *I. belvuensis* Reeside. Some 75 feet higher in the section, in the Mancos shale, *Gryphaea newberryi* Stanton and *Inoceramus labiatus* occur, and 200 to 300 feet higher still, the *Prionocyclus* fauna. The basal part of the Mancos shale in adjacent areas in Colorado and eastern Utah has yielded *Exogyra suborbiculata, E. columbella* Meek, *Metoicoceras whitei*, and a species of *Mammites* (*Pseudaspidoceras?*). An interesting species at this horizon a little farther west is *Exogyra olisiponensis* Sharpe. The *Prionotropis woolgari* fauna has not been recognized in this second area.

The similarity in the sequence of faunas in the two areas makes it likely that the age of the beds containing the *Acanthoceras* is nearly the same and that the deposition of sandstone at the western locality began sometime after it had ceased at the eastern locality, the intervening time being represented by the 60 feet of lower Graneros shale between the *Acanthoceras* horizon and the Dakota sandstone.

The genus *Acanthoceras*, in the strict sense, has been universally considered to characterize the Cenomanian part of the Upper Cretaceous, and such species as *Metoicoceras whitei* the lower Turonian. The occurrence of *Acanthoceras* in the Western Interior region permits a more definite age assignment of the containing beds and a more definite correlation with the Gulf region and with other areas outside the United States.

PROCEEDINGS OF THE ACADEMY AND AFFILIATED SOCIETIES

ENTOMOLOGICAL SOCIETY

393D MEETING

The 393d regular meeting was held May 5, 1927, in Room 43 of the National Museum. President J. A. HYSLOP presided. There were present 21 members and 13 visitors.

On request Dr. CARL JORDAN of the Tring Museum, a specialist in Lepidoptera, but who now has in preparation a monograph on fleas, discussed some of his recent work, contrasting it with former activities and dwelling upon some of the marked differences in the two lines of research. He reported that his monograph is well under way and he now has under consideration some seven hundred known species of fleas. He also touched on recent general studies by various investigators in Europe and America on the interrelationships of insects with other animal forms.

Dr. HOWARD, in commenting on Dr. Jordan's address, emphasized the importance of his work, and referred to their associations together in company with Dr. Schauss at the Oxford Congress, and expressed hope that Dr. Jordan would be here again in 1928.

Upon request another visitor, F. C. BISHOPP, of the Bureau of Entomology located at Dallas, Texas, expressed his pleasure at being able to attend a meeting of our society and at the prospect of being able soon to attend these more regularly.

Program: Dr. W. E. DOVE and Dr. G. F. WHITE: *The creeping eruption.* (Illustrated.) It was pointed out that creeping eruption as defined in most text books is a human skin disease due to the migration of fly larvae in the skin. The recovered larvae in some instances have been identified as those of *Gastrophilus,* in others as *Hypoderma.* In still other cases no larva was found. There is, therefore, not a single creeping disease but a number of them. One of these creeping diseases occurring in the South Atlantic and Gulf States has been shown to be due not to a fly larva but to the larva of a nematode. It has been demonstrated further that the nematode in this instance is *Ancylostoma braziliense,* one of the dog and cat hookworms. Out of twenty-seven street dogs examined in Jacksonville, Florida, twenty-six were found infected with this worm. The number of worms harbored by each dog varied from near fifty to more than five hundred. The potential infestation of an area is further indicated by the fact that each female worm may lay up to five thousand eggs per day.

Discussed by EWING, GAHAN, BAKER, BISHOPP, HOWARD, and HYSLOP.

Dr. P. W. MASON: *A discussion on the specialization of aphids from general feeders to monoxenous feeders.* Evidence shows that aphids originated in north temperate regions. These early, primitive forms were general feeders on any existing vegetation. From these heteroxenous feeders, they gradually evolved to dioxenous feeders, which condition is normal at the present time. The next step will probably be to that of monoxenous feeders. Several examples were given of species which have already learned to live on one host, some of them having so lived since Tertiary times, when the alternate host was destroyed by glaciation. When migration finally ceases, each species which is now dioxenous will probably evolve into two species, one on the present primary and one on the present secondary host, if each host continues to exist.

Discussed by HYSLOP and BAKER.

Dr. ALDRICH reported the recent accession by the National Museum of a collection of Lepidoptera made by Henry F. Schoenborn, containing considerable European material noteworthy for range of distribution and for being especially well mounted. He also directed attention to and commented on a recently issued paper by C. H. T. Townsend, entitled "Synopse dos generos muscoideos da região tropical de America, com generos e especies novas." Dr. Aldrich further stated that he had for distribution on request separates of his recent Presidential address on "Limitations of taxonomy."

Dr. HOWARD stated that a letter just received from R. B. Coad at Tallulah, La., reported that though the laboratory force was safe, the flood waters were standing ten feet in depth all over the city of Tallulah, that airplanes recently used in boll weevil work were being used in flood rescue work. Some very interesting airplane photographs of the flooded areas were sent, showing refugees on elevations greatly resembling work of prehistoric mound builders. This suggested possibility that some of these mounds originally might have been constructed for use in periods of flood.

Dr. BAKER reported the recent finding in Texas of the Mexican fruit fly or orange maggot, *Anastrepha ludens*, formerly *Trypeta ludens*.

H. S. BARBER showed a map and discussed an apparently unrecorded trip made by Thomas Say into old Mexico. He quoted Dr. Schwarz's remark—"So! Say went to Mexico! I did not know that before"—made more than twenty years ago while discussing Thomas Say's remarks on the nest and honey of the types of his *Polistes mellifica* from near Jalapa, and on the behavior of the Indians from whom Say had obtained them. A number of other remarks by Say, occurring in various papers on shells, insects, and aboriginal artifacts were cited, indicating that about 1828 Thomas Say had collected at Vera Cruz, Jalapa, Mexico City, Tacuba and Chalco. Mr. Barber believes that the type localities of most of the species described by Say with the simple statement "Inhabits Mexico" are either in the vicinity of the City of Mexico, or along the old road from Vera Cruz to the capital. He showed a trail map of the routes and dates of Say's travels in so far as he had been able to learn them, which is expected to appear with more detailed notes in Entomological News.

Dr. H. MORRISON directed attention to a meeting next week of the Indiana Academy of Sciences to be held at New Harmony, Indiana, the former home of Thomas Say, at which meeting this fact and Say's relation to American entomology would be emphasized.

J. S. WADE, *Recording Secretary.*

SCIENTIFIC NOTES AND NEWS

LAURENCE LA FORGE has resigned as geologist in the U. S. Geological Survey.

S. F. SCHAIRER, graduate student in the department of chemistry at Yale University, has joined the staff of the Geophysical Laboratory, Carnegie Institution of Washington.

CHARLES E. RESSER and R. S. BASSLER have returned from a field-study undertaken for the purpose of securing data necessary to complete a manuscript on the stratigraphy of the Cambrian of the Rocky Mountain region, left unfinished by the late Dr. C. D. Walcott. Their expedition traveled by motor-truck from the Wasatch Mountains in Utah to Alberta and British Columbia, and visited areas of Cambrian rocks at many places along the route.

IRWIN R. POHL, Division of Paleontology, U. S. National Museum, spent six weeks in July and August, in coöperation with the Milwaukee Public Museum, in a study of the lower Devonian of the lower Peninsula of Michigan and adjacent areas.

W. F. FOSHAG and HARRY BERMAN have completed a trip to mining districts in northern Mexico, conducted under the auspices of the U. S. National Museum and the Mineralogical Museum of Harvard University, for the purpose of collecting exhibition specimens of the minerals of the region.